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The field-ionization of near-dissociation ion-pair states of I_2

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Using a resonant multiphoton excitation pathway, it is shown that electronic states down to 30 cm^{-1} below the first ion-pair dissociation threshold of I_2 can be efficiently converted from initially prepared well-defined low- J states to long-lived ($\tau_d > 4\text{ }\mu\text{s}$), subthreshold zero ion kinetic energy (ZIKE) ion-pair states which are analogous to high, zero electron kinetic energy, Rydberg states. A pulsed electric field is used to dissociate the ZIKE states and produce free-ion pairs (i.e., $I^+ + I^-$). Direct excitation to very high vibrational levels of the ion-pair states is ruled out and polarization data are used to probe the spectroscopic character of the doorway states to free-ion formation. The ion-pair dissociation limit, determined from the extrapolation to zero field of the onset of the prompt I^+/I^- signal, agrees well with the literature value. © 2002 American Institute of Physics. [DOI: 10.1063/1.1503777]

I. INTRODUCTION

Only about 50 examples of photodissociative ion-pair formation, $AB + h\nu \rightarrow A^+ + B^-$, are known¹ even though this channel is available to all molecules if the anion B^- is stable to autodetachment. Following on the success of threshold photoelectron spectroscopy, Martin and Hepburn^{2,3} found that subthreshold ion-pair states are long-lived states analogous to high- l , zero electron kinetic energy (ZEKE), Rydberg states.⁴ They designated the technique threshold ion-pair production spectroscopy (TIPPS) and applied it to the study of O_2 (Ref. 2) and HCl .³ The exact analogy between these stabilized ion-pair states and the precursor ZEKE states (where the vibrational quantum number, v , of the former is analogous to the principal quantum number, n , of the Rydberg state) suggests calling them ZIKE (zero ion kinetic energy) states.

The work on O_2 and HCl , as well as subsequent studies^{5,6} on H_2 , D_2 , and H_2S , involved single-photon excitation to ionic dissociation limits which lie above the first ionization energy (IE) of each molecule. In a previous paper,⁷ we have shown that multiphoton pathways can be used to access the ZIKE states of ICl , which were then detected in the I^+ or Cl^- mass channel by pulsed-field dissociative ionization. In ICl , as in most of the halogens, interhalogens and alkyl halides, the ion-pair threshold lies below the molecular IE. The atomic ion production channels are highly structured both above and below the free-ion threshold, indicating the role of doorway states which are coupled to the dense manifold of ion-pair states just below threshold and the continuum above.

In the present work we investigate the near-dissociation region of the ion-pair states of I_2 where the ion-pair thresh-

old is again below the molecular IE. In these multiphoton excitation experiments, small dc fields are applied during the “zero-field” time delay period in order to determine the ion-pair dissociation limit from the extrapolation to zero field of the onset of the ion signal. Previous threshold ion spectra were usually only recorded in the positive ion channel.^{2,3,5,6} The spectra to be presented here could be equally well recorded in either the I^+ or I^- channel. The I^- signal was recorded as it has the advantage of not being swamped by ions produced by photodissociation of the parent molecular ion, I_2^+ , and hence a discrimination field is not necessary, unless it is used to further explore the ZIKE states.

II. EXPERIMENT

The apparatus comprised a dual laser system, a pulsed molecular beam, a time-of-flight (TOF) mass spectrometer, and signal collection electronics. The laser system consisted of two independently tunable dye lasers (a Lambda Physik FL3002 and a Lambda Physik FL2002) pumped by a XeCl excimer laser (a Lambda Physik EMG201MSC). The fundamental, ν_1 , and frequency doubled, ν_2 , outputs of the dye C153 were introduced collinearly into the ionization chamber via a 6 cm focal length lens. The visible radiation and its frequency doubled output were focused at slightly different distances from the lens. The lens was positioned such that the visible output was focused in the detection region of the TOF mass spectrometer whilst the UV output was slightly defocused at this point. In addition, the frequency doubling crystal was slightly detuned from its optimum doubling angle. Both measures were taken to produce the correct balance of laser powers to achieve the required excitation pathway. The fundamental output of C153, from a second laser, provided the probe photon, ν_3 . This was directed into the chamber at 180° to the pump beams via a second 6 cm focal length lens. This lens was positioned such that the foci of the

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visible outputs of the pump and probe lasers coincided. Laser wavelengths were calibrated from the I_2 fluorescence excitation spectrum.

The two counterpropagating dye laser beams intersected the molecular beam at 90° between two electrodes separated by a distance of 1.6 cm. A high positive or negative potential was applied to the upper electrode, while the lower electrode at the entrance to the TOF tube was grounded. The lower electrode contained a 1.5-mm-diam pinhole through which ions passed before entering the 52-cm-long flight tube which was terminated by a microchannel plate (MCP) detector. For the field-induced dissociation experiments, a high voltage pulse (1.25 kV/cm) with a 20 ns rise time and a duration of 2 μ s, at a variable time delay after the laser pulse, was used to complete the dissociation of any long-lived ion-pair states just below dissociation. This field, according to its direction, also served to accelerate positive or negative ions into the flight tube. A variable dc voltage of up to ± 30 V could also be applied to the upper electrode.

The TOF profiles were recorded on a Lecroy 9344 digital oscilloscope. The excitation spectra were recorded by processing the signal from the MCP detector with a Stanford Research SR250 boxcar and storing it on a PC.

The pulsed jet system was of conventional design and employed a commercial pulsed valve (General Valve, nozzle diameter 250 μ m). Helium or argon at a pressure of 200–400 Torr was passed over solid I_2 at room temperature and the resulting mixture of I_2 and carrier gas expanded through the nozzle.

III. RESULTS AND DISCUSSION

A. Ion-pair formation using three-color multiphoton excitation

Ion-pair formation from I_2 using multiphoton excitation was investigated in a two-laser, three-color experiment using a dye laser fundamental, ν_1 , and its frequency doubled output, ν_2 , ($2\nu_1$) to pump $\nu=168$ of the $E(0_g^+)$ ion-pair state via $\nu=20$ of the $B(0_u^+)$ state, through an accidental double resonance. The third color was used to probe the energy region around the first threshold for ion-pair formation, by scanning ν_3 in the range 18 000–19 000 cm^{-1} , as illustrated in Fig. 1. An accidental resonance in which $\nu_1 \approx 17\,900\text{ cm}^{-1}$ was chosen because the total three-photon energy ($\nu_1 + \nu_2 + \nu_3$) lies below the ion-pair formation threshold. Thus, competition between ion-pair formation by absorption of a second ν_1 photon and a ν_3 photon at the third step can be minimized.

In the present experiment, an accidental resonance occurs when ν_2 is exactly equal to the energy of an allowed transition between rovibronic levels of the $B(0_u^+)$ and $E(0_g^+)$ states and ν_1 lies within $\pm 2\text{ cm}^{-1}$ of a transition which excites the appropriate rovibronic level in the $B(0_u^+)$ state from the ground state. Under these circumstances, there is some ν_1 radiation that comes from the tail of the laser line, and is hence very weak, that can excite the very efficient pump stage. In a pulsed molecular beam (jet-cooled) experiment, only accidental resonances involving low J levels are observed strongly. When the same energy region is studied via

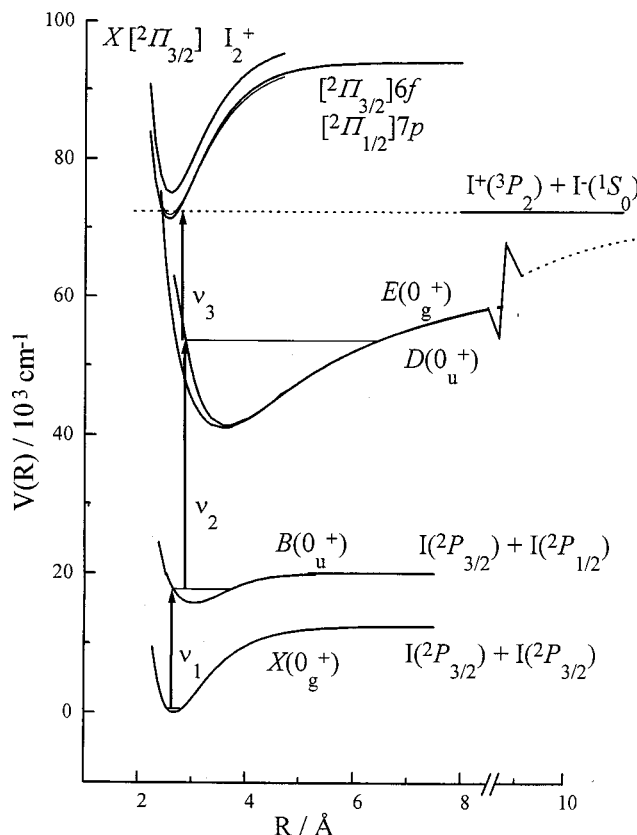


FIG. 1. The multiphoton excitation pathway via $\nu=20$ of the $B(0_u^+)$ and $\nu=168$ of the $E(0_g^+)$ states of I_2 . Also shown are typical Rydberg states which can act as doorway states to free-ion formation.

fluorescence in a static cell at room temperature, a very different picture emerges. The strong accidental resonances observed in a jet-cooled experiment are now all very weak, less than one-tenth of the intensities of the strongest bands. The latter are now optimized double resonances, i.e., the pump step is excited by radiation that comes from the peak of the ν_1 laser line and not from the wing. These optimized double resonances involve high J levels which have very low populations under jet-cooled conditions.

One result of this analysis of the jet-cooled spectrum is that the two-photon transition energy is not exactly equal to $3\nu_1$. In an experiment in which the ion-pair dissociation threshold is to be measured, the crucial factor is the total energy of the J level populated in the intermediate ion-pair state. This can be determined most accurately by a rotational band contour simulation of the $E(0_g^+) \leftarrow B(0_u^+)$ transition, from which it was shown that the rotational level accessed in the $E(0_g^+)$ state is $J \approx 13$. Using the known term value of $53\,675.5\text{ cm}^{-1}$ for $\nu=168$ of this state⁸ and an estimated B value of 0.014 cm^{-1} , it was calculated that this J level is $53\,678.0\text{ cm}^{-1}$ above $\nu=0, J=0$ of the ground state. The error limits on this value, arising from the uncertainties in the term value, the B value and the numbering of the J level are estimated to be $\leq \pm 2\text{ cm}^{-1}$. This is the dominant source of the error limits of the observed free-ion dissociation threshold values.

The I^+ and I^- production spectra are shown in Fig. 2. The first ion-pair threshold for I_2 is calculated to occur at

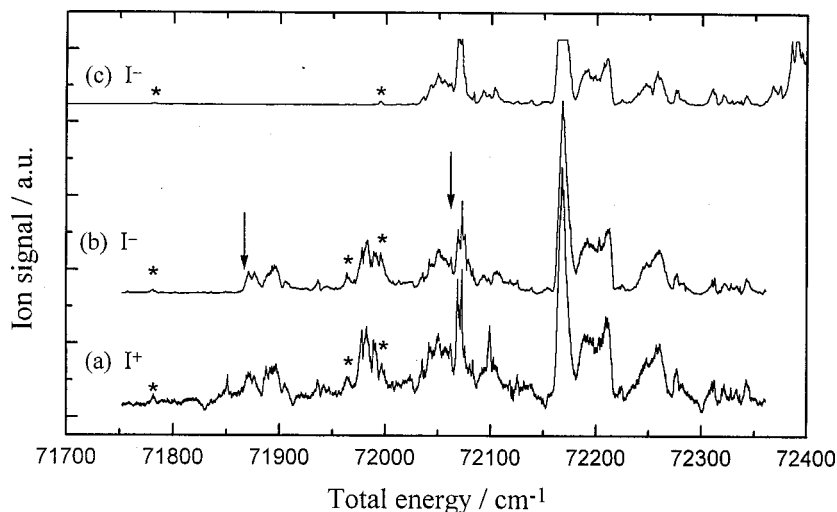


FIG. 2. The three-color free-ion formation spectrum of I_2 recorded via the I^+ (a) and I^- (b) mass channels with no delay on the extraction pulse; in (c) the extraction pulse was delayed by 385 ns. The energy scale is relative to $\nu=0, J=0$ of the ground state. The field-free and field-induced thresholds are marked by arrows. Asterisks denote weak bands due to $(\nu_3 + \nu_2 + \nu_3)$ transitions.

$72\,062\text{ cm}^{-1}$, using the literature values^{9–11} for the IE of I, $84\,295\text{ cm}^{-1}$, the electron affinity of I, $24\,673\text{ cm}^{-1}$, and the dissociation energy of the ground state of I_2 , $12\,440\text{ cm}^{-1}$. The I^- spectrum in Fig. 2(b) shows a clear onset at $71\,864\text{ cm}^{-1}$, $\sim 200\text{ cm}^{-1}$ below this field-free value of the lowest ion-pair formation threshold. This value is consistent with the decrease expected from the applied field, F , of 1.25 kV/cm according to the usual $6F^{1/2}$ electric field dependence observed in ZEKE spectroscopy. Above the threshold, the spectra of I^+ and I^- are almost identical, but the I^+ signal continues, albeit weakly, in the energy region below the field-lowered threshold where, on energetic grounds it can only be formed by the absorption of another photon to a dissociative state of I_2^+ . The fact that there is very little I^+ ion signal below the threshold in the spectrum shown in Fig. 2(a) is due to there being only a few resonant intermediate states available to assist the photoionization process. Above threshold, the I^+ and I^- signals are of roughly equal intensity, indicating that the ion-pair dissociation channel is the dominant process in this region. The highly structured spectrum, with little or no continuum ion-pair production between individual peaks, indicates the crucial role of doorway

states in the ion-pair formation process. The features marked with an asterisk in Fig. 2 are caused by two-color (ν_3 and ν_2 only) signals.

The highly structured ion-pair spectra of I_2 , recorded in both the I^+ and I^- mass channels, reveal the presence of doorway states that are coupled to the dense manifold of near-dissociation vibrational levels of ion-pair states converging on the first dissociation limit of $I^+(^3P_2) + I^-(^1S_0)$, when below this threshold, and equally to the ion-pair continua when above. Using the present intermediate state, only 0_u^+ and 1_u doorway states can be accessed and the ion-pair states to which they are coupled, assuming homogeneous coupling, must be the $D(0_u^+)$ and $\gamma(1_u)$ states.

Polarization data can give further insight into the nature of the doorway states. Figure 3 shows the TOF profile of the I^+ signal following a three-photon excitation of $72\,267\text{ cm}^{-1}$, $\sim 200\text{ cm}^{-1}$ above the dissociation threshold after a delay of 700 ns. The polarization experiments were carried out with the two pump photons, ν_1 and ν_2 , always polarized perpendicular to each other. This produces a broad, though not quite isotropic, distribution of m_J sublevels of the $E(0_g^+)$

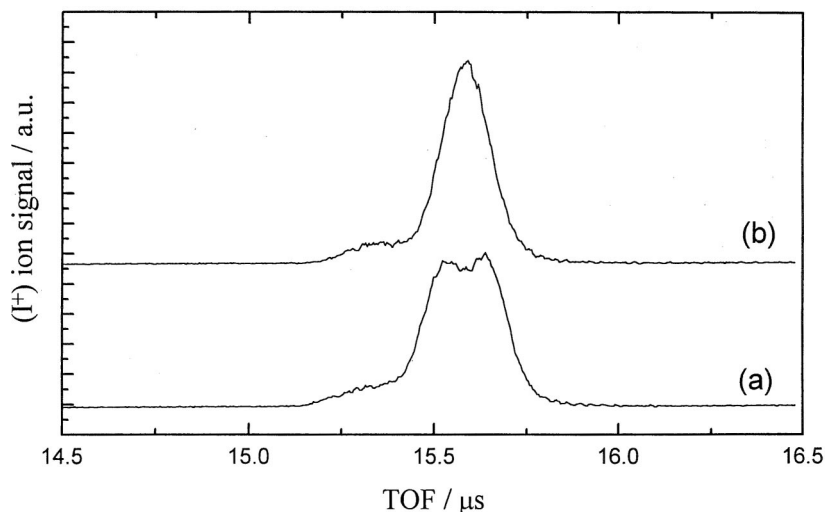


FIG. 3. TOF profiles of the I^+ signal recorded following excitation $\sim 200\text{ cm}^{-1}$ above the free-ion formation threshold using probe photons which were polarized parallel (a) and perpendicular (b) to the TOF axis. The extraction pulse was delayed by 700 ns.

state, as can be seen from the very similar areas under the two TOF spectra when the plane of polarization of the probe photon is turned through 90° .

The fast and slow arrivals of the double-peaked TOF profile shown in Fig. 3(a) are characteristic of free ions, created with kinetic energy by photolysis, that are initially moving either toward (slow), or away from (fast), the entrance to the flight tube. This was recorded with the electric vector, ϵ , of the probe photon parallel to z , the TOF axis. When ϵ of the probe photon is perpendicular to z , the bimodal TOF spectrum is replaced by a single-peaked one, as shown in Fig. 3(b). If the probe transition is a perpendicular one and $\epsilon \parallel z$, molecules with $\mathbf{J} \parallel z$ (high m_J states) are preferentially dissociated, scattering the ions largely perpendicular to z and hence leading to a single-peaked TOF profile. If the probe transition is a parallel one, molecules with $\mathbf{J} \perp z$ (low m_J states) are preferentially dissociated, leading to scattering predominantly in the $\pm z$ direction and hence a bimodal TOF profile. If ϵ is perpendicular to z , the above-mentioned patterns are reversed, the bimodal distribution now being associated with a perpendicular final transition. A bimodal TOF spectrum is clearly seen when $\epsilon \parallel z$, indicating a parallel transition. The profiles shown in Fig. 3 were recorded using a single transition chosen at random; a more systematic study will have to be undertaken to see if all of the doorway states, accessed from this particular intermediate state, have 0_u^+ symmetry.

If, as seems likely, the doorway states are Rydberg in nature, then they must be np or nf states where $n \geq 10$ and 6, respectively, if the states have a ground state, $^2\Pi_{3/2}$, ionic core and $n \geq 7$ and 4, respectively, if they have a spin-orbit excited, $^2\Pi_{1/2}$, core. The doorway states could also be ion-pair states from a higher energy cluster, e.g., those dissociating to $\text{I}^+(^3P_{0,1}) + \text{I}^-(^1S_0)$, or even one of these mixed with a Rydberg state, a three state interaction. However, one type of transition which is apparently not seen is that going directly to the long-lived ion-pair levels $\sim 30 \text{ cm}^{-1}$ below threshold, $E(\nu \approx 10^4) \leftarrow E(\nu = 168)$, the transition which is the strict analog of the ZEKE experiment.

B. The lifetime of ZIKE states

The I^- spectrum was also recorded with the high voltage pulse delayed by 385 ns, i.e., a relatively short time after the laser pulse, and is shown in Fig. 2(c). By comparison with the spectrum recorded without a delay shown in Fig. 2(a), it can be seen that even at such a short delay, all structure up to $\sim 30 \text{ cm}^{-1}$ below threshold has already disappeared. The ion signal continues above the field-free threshold because the ions are created with kinetic energies that are insufficient to move them, in 385 ns, to a position in space that will result in a flight time that is significantly different from that of the ZIKE ions.

Similar spectra showing structure to $\sim 30 \text{ cm}^{-1}$ below threshold were recorded with a pulsed field delayed by up to 5 μs . However, even this may not be a measure of the real lifetime of the ZIKE states since there is a loss of signal due to the movement of the excited molecules out of the detection region of the TOF, in the direction of the motion of the

molecular beam. It is estimated that the molecules will have traveled approximately 2 mm in 4 μs which should be compared with the 1.5 mm aperture through which the ions are collected. When He, at the same backing pressure as Ar, was used as the carrier gas, it was found that ZIKE ions can only be observed with delays less than 2 μs . In the Ar expansion, the molecules travel with a lower postexpansion velocity and hence spend a longer time in the detection region.

These delayed pulsed-field dissociation experiments show the existence of long-lived ($>4 \mu\text{s}$) ion-pair states of I_2 down to 30 cm^{-1} below the dissociation limit. In ICl , they have been observed 50 cm^{-1} below the limit.⁷ These states are analogous to the high lying ZEKE Rydberg states which have been observed down to only 10 cm^{-1} below the ionization energy. The conversion of the Rydberg doorway states into these long-lived states is favored by the high density of ion-pair vibronic levels. An important difference between threshold heavy ion states and their electronic counterparts (Rydberg states with $n \geq 100$) is that, since the effective Rydberg constant is proportional to the reduced mass of the ion pair, there is a much greater density of states at a given energy below threshold in the case of ion-pair states. For example, at a binding energy of $\sim 10 \text{ cm}^{-1}$, the density of high- ν ion-pair states is 200 times higher than that of high- n Rydberg states.

A further consequence of the larger reduced mass in threshold ion-pair states is that the period of vibration is much greater, leading to much longer lifetimes even before conversion to high- J states. Taking a lower limit to the lifetime as the vibrational period $\tau = h \delta n / \delta E$, corresponding to the ion-pair state decaying if the ions return to the inner turning point of the rectilinear motion ($J=0$), we find $\tau = 58 \text{ ns}$ for a state 10 cm^{-1} below dissociation and $\tau = 1.8 \mu\text{s}$ for a state 1 cm^{-1} below dissociation. One might thus expect lifetimes of this order of magnitude even in the absence of any conversion to high- J states. However, in the present work, time delays up to 5 μs are used and therefore we must be dealing with very high- J states.

C. Measurement of the free-ion formation threshold

Delayed pulsed-field dissociation experiments were carried out using a delayed $\pm 1.25 \text{ kV/cm}$ high voltage pulse (+ for cations and - for anions) superimposed on a constant small dc voltage (0 to $\pm 30 \text{ V}$). This dc field lowers the dissociation threshold producing pairs of ions with low translational energy. Ions formed in this way, or by excitation above the field-free threshold, during the duration of the laser pulse will subsequently be referred to as prompt ions. The small dc field also pushes all the prompt ions of a selected polarity, whether initially moving toward or away from the entrance to the flight tube, toward the entrance of the flight tube, before the high voltage acceleration pulse is applied. With our experimental arrangement, this results in a longer arrival time due to the lower potential drop experienced by these ions. ZIKE states which lie below the dc field-lowered threshold are resistant to small-field ionization and are only ionized later by the large pulsed field giving rise to a TOF peak whose arrival time is invariant with the ap-

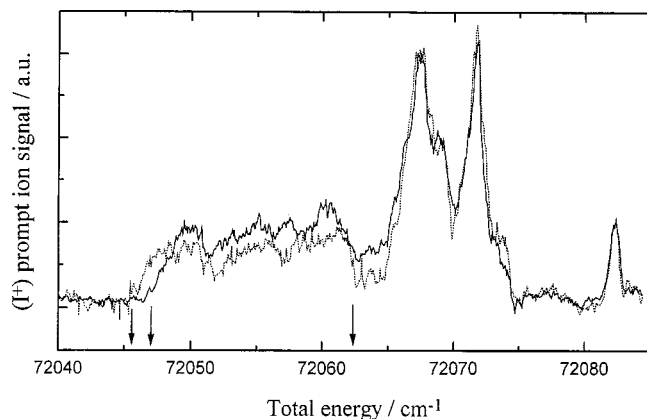


FIG. 4. The prompt I^+ ion spectrum recorded as a function of an applied dc field; 7.81 V/cm (solid line) and 9.38 V/cm (dotted line). The 1.25 kV/cm extraction pulse was delayed by 3.5 μ s. The two field-induced and the field-free thresholds are marked by arrows.

plied dc field. Ions observed in this way will be referred to as ZIKE ions. Thus, the boxcar can be gated, uniquely, on either prompt or ZIKE ions.

In the conventional TIPPS experiment, the free-ion threshold is measured by the extrapolation to zero field of the observed high-energy maximum of the ZIKE ion signal. The free-ion threshold of diatomics can also be determined from the prompt ion signal. The prompt I^+/I^- ions that are created at threshold with essentially zero relative velocity show a characteristic shift of energy threshold with the small applied dc field, F . This shift can be extrapolated to determine the zero-field threshold. Figure 4 shows two spectra taken with different values of F . The red edge at threshold is well defined and a plot of threshold energy against $F^{1/2}$, for values of F between 4 and 12 V/cm, is linear with a slope of 5.4, yielding a zero-field threshold energy of 72062 ± 2 cm^{-1} , which agrees well with the literature value.

A sharp onset in the prompt ion spectrum can only be effectively observed in a multicolor experiment where the final transition originates from a single well-defined rotational level. In one-photon or nonresonant one-color multiphoton experiments, transitions from rotationally excited molecules in the ground electronic state will blur the ion-pair threshold unless, as in the case of the lighter diatomics, the individual threshold $\leftarrow J''$ transitions can be resolved.² Although quite a sharp onset in the prompt ion spectrum is observed in the present experiments, the conditions under

which a single rovibronic level is populated after the two pump steps are only approximated because an accidental double resonance is used. Population of a single rovibronic level could be achieved by having all three photons independently tunable in a three-laser arrangement. This will result in a more flexible experiment which will yield more accurate threshold values.

IV. CONCLUSION

It has been demonstrated that electronic states down to 30 cm^{-1} below the first ion-pair dissociation threshold of I_2 can be efficiently converted to long-lived (>4 μ s), sub-threshold ion-pair, ZIKE, states which are analogous to high Rydberg, ZEKE, states. By collecting negative ions it was possible to use one less applied field than in previous TIPPS experiments where positive ions were collected. It has been shown that polarization data can be used to probe the spectroscopic character of the doorway states which are necessary for the observation of free-ion formation. The ion-pair dissociation limit was determined from extrapolation of the field-dependent onset of the prompt ion signal. We propose that the multiphoton approach used here, in which the need to generate vacuum ultraviolet or extreme ultraviolet laser photons is avoided, can be further applied to this area of ion-pair spectroscopy.

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